CHEMICAL CHARACTERIZATION OF SHALE OIL AND RELATED FUELS

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INTRODUCTION

In view of the recent activity directed towards the production of fuel oils as a substitute for natural petroleum products, there has arisen a need for chemical characterization of these materials. Chemical characterization of new fuels is important not only in order to provide an understanding of their chemical and physical properties, but also to provide preliminary data from which their potential environmental impact may be judged.

The results reported here represent a preliminary analytical survey of the organic constituents of shale oil, synthoil, and Prudhoe Bay crude oil, as a prelude to the comprehensive analytical intercomparison which will be reported subsequently. The analytical techniques employed in this study are liquid chromatography (LC), Fourier transform infrared spectroscopy (FTIR), and gas chromatographic-mass spectrometry (GC-MS). The analytical procedures used are similar to those described in a recent EPA publication[1] "Technical Manual for Analysis of Organic Materials in Process Streams", with regard to Level I analysis.

EXPERIMENTAL AND RESULTS

Liquid chromatography was carried out using 25 x 250 mm columns packed with 80 g of >200 mesh silica gel, which had been activated at 200 C for over 24 hours. The columns were pre-eluted with 200-ml methanol, 200-ml methylene chloride, and finally 200-ml 60/80 petroleum ether. Aproximately 2.0 g of shale oil, synthoil, and Prudhoe Bay crude oil were separately dissolved in 25-ml 60/80 petroleum ether, and any insoluble residue was removed by centrifuging. Each oil was separately eluted on a silica gel column, using the following elution profile:

Fraction	Eluent
1	200-ml petroleum ether
2	200-ml 20% methylene chloride in petroleum ether
3	200-ml 20% methylene chloride in petroleum ether
4	400-ml 20% methylene chloride in petroleum ether
5	400-ml methylene chloride
6	400-ml 10% methanol in methylene chloride
7	400-ml methanol

Following elution and reduction in volume of each of the fractions by Kuderna-Danish evaporation, 1% of each fraction was used to determine the weight of material in each fraction after complete evaporation of the solvent by this procedure. Thus, the weight of material present in each fraction was calculated to be as follows:

Weight of Material (g) in Each LC Fraction

	1	2	3	4	5	6	7	Petroleum Ether Insoluble	Original Sample
Shale Oil	0.50	0.37	0.12	0.06	0.19	0.50	0.10	0.06	2.00
Prudhoe Bay	0.81	0.43	0.11	0.04	0.06	0.07	0.02	0.08	2.01
Synthoil	0.13	0.46	0.21	0.04	0.15	0.18	0.06	0.81	2.02

Previous knowledge of the type of organic compounds which are typically observed in the fractions of this LC separation scheme permits the following introductory observations.

(1) The hydrocarbon content of shale oil is somewhat similar to Prudhoe Bay Crude, with slightly lower aliphatic content. There are substantially larger quantities of highly polar materials in shale oil.

(2) Synthoil contains far less aliphatic hydrocarbons than either shale oil or Prudhoe Bay crude; its hydrocarbon content being largely aromatic. It contains less polar materials than shale oil, but more than Prudhoe Bay crude oil.

FTIR analysis of a thin film of material from each fraction was subsequently carried out; the results are summarized below (shale oil = SH, synthoil = SY, and Prudhoe Bay crude oil = PR).

Fraction 1

Fractions from all three oils contained saturated aliphatic hydrocarbons; shale oil showed some evidence of olefins. The degree of branching of the hydrocarbon chains is given by

CH_3/CH_2 SH > PR > SY.

Fraction 2

Fractions from all three oils were largely saturated aliphatic hydrocarbons, with some evidence for aromatic hydrocarbons. GC-MS analysis subsequently showed that the aromatic compounds present were alkyl benzenes and alkyl naphthalenes in all cases. Again shale oil was shown to contain the most highly branched hydrocarbons, as shown by the CH_3/CH_2 ratio

CH_3/CH_2 SH >> PR > SY.

Synthoil contains substantially more aromatic hydrocarbons than either shale oil or Prudhoe Bay crude oil

Aromaticity SY >> SH ≃ PR.

Fraction 3

Shale oil and Prudhoe Bay crude exhibited considerable saturated hydrocarbon chain, with some aromatics. Synthoil showed evidence of large amounts of aromatic compounds. Prudhoe Bay crude oil showed evidence of aldehydes or ketones, while shale oil additionally showed small evidence of hydroxy compounds. The degree of hydrocarbon chain branching and aromaticity are given by

CH_3/CH_2 SH > PR >> SY
Aromaticity SY >>> PR > SH.

Fraction 3 was additionally subject to GC-MS analysis in all cases, and the distribution of polynuclear aromatic hydrocarbons (PAH) in each oil was established (see later).

Fraction 4

All three oils showed evidence for hydroxy and carbonyl compounds, in addition to strong indications of both aliphatic and aromatic hydrocarbons. Shale oil and Prudhoe Bay crude both showed considerably less aromatic content than synthoil, which in turn showed far less evidence of branched hydrocarbon chains. Shale oil showed substantially more hydroxy and carbonyl compounds than the other oils.

CH_3/CH_2	PR > SH >> SY
Aromaticity	SY >>> PR > SH
OH	SH >> PR > SY
C=O	SH >> PR > SY

Fraction 5

Shale oil and Prudhoe Bay crude both contain considerable saturated aliphatic hydrocarbons and some aromatic hydrocarbons; both contain traces of hydroxy compounds and larger amounts of carbonyl compounds. In addition to all of the foregoing, synthoil contains considerable quantities of aromatic hydrocarbons, and most probably amines and acid salts.

Aromatics	SY >>> PR > SH
CH_3/CH_2	SH ≈ PR > SY
C=O	SH ≈ PR >> SY
OH	SY >> SH > PR.

Fraction 6

All three oils showed evidence for saturated hydrocarbons, but only synthoil showing significant aromaticity. Phenols and carbonyl compounds were evident in each oil but synthoil showed additional evidence for acid salts and sulfonates. The FTIR analysis of each fraction may be summarized as follows:

Aromaticity	SY >>> PR ≈ SH
CH_3/CH_2	SY >> PR > SH
OH	PR > SY > SH
C=O	SH >> PR >> SY.

Fraction 7

In addition to saturated aliphatic hydrocarbons in all oils, there was evidence for phenols and carbonyl compounds in each fraction. Synthoil additionally showed evidence of moderate sulfonate content, while amine and amine salts were evident in shale oil. The analyses may be summarized

CH_3/CH_2	PR > SH > SY
OH	SY > PR > SH
C=O	PR ≈ SH > SY.

Summary of FTIR Analyses

The FTIR analysis of each LC fraction of shale oil, synthoil permits some general observations to be made regarding these fuels. Synthoil is by far the most aromatic in character and shale oil exhibits the greatest extent of branching in the aliphatic side chains. Shale oil contains the greatest proportion of carbonyl compounds, with synthoil containing the least. Each of the oils contains phenols, and to a lesser extent amino compounds, in similar amounts to each other.

These general findings may be briefly summarized as follows:

Fraction	Aromatic Content of Fraction
2	SY >> PR ≈ SH
3	SY >>> PR > SH
4	SY >>> PR > SH
5	SY >>> PR > SH
6	SY >>> PR ≈ SH.

CH_3/CH_2 Ratio by Fraction

Fraction	
1	SH > PR > SY
2	SH >> PR > SY
3	SH > PR >> SY
4	PR > SH >> SY
5	SH ≈ PR > SY
6	SY >> PR > SY
7	PR > SH > SY

OH or NH Content by Fraction

Fraction	
3	SH -- --
4	SH >> PR > SY
5	SY >> SH > PR
6	PR > SY > SH
7	SY > PR > SH

C=O Content by Fraction

Fraction	
3	SH ≈ PR
4	SH >> PR > SY
5	SH ≈ PR >> SY
6	SH >> PR >> SY
7	SH ≈ PR > SY

Polycyclic Aromatic Hydrocarbon (PAH) Analysis by GC-MS

Fraction 3 in all cases was shown to contain PAH compounds with molecular weight distribution between 150 and 400. Quantitative measurements were made on a large number of methyl isomers using the ion current integration technique[2], but due to the unavailability of sufficient standard reference materials the ionization efficiencies of the methyl isomers were assumed to be equal to the parent PAH compound in every case. Separation was achieved using a 6' 1 percent OV-101 column, programmed from 100 to 340 C at 4^{-1} C min^{-1}. Mass spectra were obtained using a Finnigan 3200 quadrupole mass spectrometer with a chemical ionization source. Data handling was accomplished with a Digital PDP8 mini-computer.

In absolute terms, synthoil was estimated to contain at least 10 times more PAH than either shale oil or Prudhoe Bay crude oil, by measurement of the species reported in Table 1.

PAH Content SY > PR ≈ SH

The relative differences in the distribution of methyl isomers of several PAH compounds are shown in Table 1. Shale oil exhibits a very distinctive pattern among all of the PAH methyl isomers observed, in that the maximum abundance usually occurs for the five or six methyl compound. Prudhoe Bay crude oil is somewhat similar to shale oil, and generally exhibits a maximum abundance of the methyl isomers at the four methyl compound on the average. Synthoil on the other hand shows a much lower tendency to contain a high proportion of very highly methylated species; the average most abundant methyl PAH in this fuel being the dimethyl compound, or smaller. This methyl isomer distribution is undoubtedly useful in fingerprinting different types of oil. However, the potential environmental impact of few methyl groups or many is not clear. While it is true that the addition of one or two methyl groups to a PAH nucleus tends to make the resultant molecule more

hazardous from a health standpoint, the addition of a large number of methyl groups could potentially be desirable from the standpoint of a reduced health risk and possibly increased biodegradability and photooxidation in the environment.[2]

REFERENCES

(1) "Technical Manual for Analysis of Organic Materials in Process Streams", P. W. Jones, A. P. Graffeo, R. Detrick, P. A. Clarke, and R. J. Jakobsen, EPA Publication No. 600/2-76-072.

(2) Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism, and Carcinogenesis, R. I. Freudenthal and P. W. Jones, Editors, Raven Press (New York) 1976.

TABLE 1. RELATIVE DISTRIBUTION OF PAH METHYL ISOMERS IN SHALE OIL (SH), SYNTHOIL (SY), AND PRUDHOE BAY CRUDE OIL (PR)

Methyl Groups		0	1	2	3	4	5	6	7	8	9	10
Anthracenes/ Phenanthrenes	SH	1.00	1.82	2.38	3.00	2.41	2.92	3.06	2.22	1.70	1.18	1.77
	SY	1.00	1.11	2.21	2.04	1.71	1.04	0.56	0.29	0.13	0.04	0.02
	PR	1.00	1.98	1.47	0.75	0.92	0.10	0.39	0.14	0.01	0.04	0.02
Pyrenes/ Fluoranthenes/ Benzfluorenes	SH	1.00	3.08	4.08	5.86	5.42	9.92	13.9	12.5	11.2	11.9	--
	SY	1.00	0.57	0.28	0.51	0.39	0.30	0.17	0.10	0.06	0.03	--
	PR	1.00	3.89	4.86	9.06	--	7.72	4.19	2.75	1.89	--	--
Benzanthracenes/ Chrysenes	SH	1.00	1.47	2.39	7.07	8.92	9.03	9.08	7.44	7.25	6.15	5.46
	SY	1.00	3.24	2.64	2.27	2.18	1.49	1.13	0.60	0.24	0.04	--
	PR	1.00	1.57	3.68	4.14	3.38	3.11	2.68	1.57	--	--	--
Cholanthrenes	SH	1.00	2.46	3.35	4.41	4.54	4.57	3.50	3.30	1.98	1.76	0.70
	SY	1.00	0.95	1.24	1.20	1.15	0.71	0.37	0.17	0.03	--	--
	PR	1.00	2.82	4.05	4.23	5.05	3.73	1.59	0.82	--	--	--
Benzpyrenes/ Benzfluoranthenes/ Perylenes	SH	1.00	1.77	2.96	3.54	7.27	5.73	6.35	5.27	4.58	3.46	2.58
	SY	1.00	2.25	2.86	3.30	5.50	4.29	2.64	0.86	0.23	--	--
	PR	1.00	3.93	8.61	7.54	20.1	17.83	11.66	5.66	--	--	--
Indenopyrenes/ Benz(ghi)perylenes	SH	1.00	1.50	2.21	--	2.10	--	2.11	--	2.13	2.04	1.79
	SY	1.00	0.90	0.53	0.62	0.72	0.34	--	--	--	--	--
	PR	1.00	3.78	2.33	--	1.73	1.16	--	--	--	--	--

TABLE 1. (Continued)

	Methyl Groups	0	1	2	3	4	5	6	7	8	9	10
Dibenzanthracenes/ Picenes	SH	1.00	4.60	--	6.44	6.67	6.69	--	6.60	--	6.16	5.04
	SY	1.00	2.51	3.89	3.46	2.77	1.06	0.49	--	--	--	--
	PR	1.00	1.42	2.36	5.69	3.61	2.35	0.47	--	--	--	--